Transport through molecular junctions with a nonequilibrium phonon population

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The calculation of the nonlinear conductance of a single-molecule junction is revisited. The self energy on the junction resulting from the electron-phonon interaction has at low temperatures logarithmic singularities (in the real part) and discontinuities (in the imaginary one) at the frequencies corresponding to the opening of the inelastic channels. These singularities generate discontinuities and logarithmic divergences (as a function of the bias voltage) in the low-temperature differential conductance around the inelastic thresholds. The self energy also depends on the population of the vibrational modes. The case of a vibrating free junction (not coupled to a thermal bath), where the phonon population is determined by the bias voltage is examined. We compare the resulting zero-temperature differential conductance with the one obtained for equilibrated phonons, and find that the difference is larger the larger is the bare transmission of the junction and the product of the electron dwell time on the junction with the phonon frequency.

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Electrons passing through a small molecule can change its quantum state and this usually requires a finite energy transfer from the transport electron, yielding interesting structures in the I-V characteristics. This rich pattern depends on featuress such as the equilibration time of the vibrations compared to the typical time between consecutive electrons passing through the junction, or whether the electrons can pump more and more excitations into the vibrational states. Single-molecule junctions based on direct bonding of a small molecule between two metallic electrodes seem by now rather established experimentally.[1–11] There are also quite a number of theoretical studies, focusing on various regimes of the relevant parameters.[12–27] In particular, the modification of the differential conductance at the opening of the inelastic channel has been an issue of considerable interest (an extended discussion may be found in Ref. 28).

An electron crossing the molecular bridge can do so with or without changing the vibrational excitation state of the molecule. At low temperatures, the first inelastic channel comes in when the bias voltage, V, exceeds $\hbar\omega_0/e$, where ω_0 is the normal frequency of the junction. This however does not necessarily imply an increase of the total conductance, since the elastic conduction channel is modified as well. Technically, the low-temperature conductance associated with the opening of the inelastic channel stems from two sources. The first is the imaginary part of the junction self energy, induced by the interaction with the oscillator. This function develops discontinuities, so that there appear additional contributions to the conductance only for $eV > \hbar\omega_0$. Discontinuities in the imaginary part of the self energy imply logarithmic divergences in its real part, via the Kramers-Kronig relations.[25,28] As a result, the low-temperature differential conductance develops logarithmic singularities (as a function of the bias voltage) around the inelastic thresholds.[14,17,25] The second contribution is due to a nonequilibrium population of the vibrations. At zero temperature, phonons can be excited only when the energy of the electrons (i.e., eV) exceeds ω_0, leading to an additional modification of the conductance at these voltages.

In a recent publication[28] we have presented a detailed calculation of the differential conductance and analyzed its behavior at low temperatures. Our calculation implicitly assumed that the molecular junction is in a good contact with a thermal bath, such that the vibrations follow the Bose-Einstein distribution, with the same temperature as the two leads. In particular we have considered the conditions for the conductance to increase or decrease at the channel opening. In this short communication we repeat that analysis for the case of a free junction (i.e., the oscillator is not coupled to a heat bath), for which at low temperatures the phonon population is determined by the bias voltage. This case is analogous to the magnetization of a Kondo ion out of equilibrium.[29]

In this note we use the same Hamiltonian and the same notations as in our previous paper.[28] To lowest order in the electron-phonon interaction on the dot, γ, the scattering-down rate (de-exciting the vibration) can be derived from the golden-rule,

$$w_{\rm down} = \gamma^2 \frac{\pi}{2} \int d\omega \mathcal{N}(\omega)\mathcal{N}(\omega+\omega_0) \times \sum_{\alpha,\alpha'=L,R} f_\alpha(\omega)\Big(1-f_{\alpha'}(\omega+\omega_0)\Big)\,, \qquad (1)$$

and the scattering-up rate, $w_{\rm up}$, is obtained from Eq. (1)

by swapping ω_0 and $-\omega_0$. Here, $f_\alpha(\omega) = (\exp[\beta(\omega - \mu_\alpha)] + 1)^{-1}$ is the Fermi distribution in the left ($\alpha = L$) or the right ($\alpha = R$) lead, in which the chemical potential is μ_α, and $\mathcal{N}(\omega)$ is the bare density of states on the dot,

$$\mathcal{N}(\omega) = \frac{\Gamma_0/\pi}{\omega^2 + \Gamma_0^2} \ . \tag{2}$$

It is assumed that the dot, modeled by a single level of energy ϵ, is coupled symmetrically to the two leads, with Γ_0 being the bare resonance width and $eV = \mu_L - \mu_R$, with $\mu_L > \mu_R$. All electronic frequencies (using $\hbar = 1$) are measured from $\epsilon - \mu$, where $\mu = (\mu_L + \mu_R)/2$. The kinetic equation for the vibration population, $N_{\rm ho}$, is then (see also Ref. 17)

$$\frac{dN_{\rm ho}(t)}{dt} = -N_{\rm ho}(t) w_{\rm down} + [1 + N_{\rm ho}(t)] w_{\rm up} \ . \tag{3}$$

The scattering-up rate is due to all processes by which an electron can excite an oscillator mode, losing the energy ω_0 in the process, and moving over from the left (right) lead back into the left (right) lead, or from the left (right) lead into the right (left) one. Hence, at zero temperature, $w_{\rm up} \neq 0$ only when the bias voltage exceeds the frequency ω_0, resulting from the $L \to R$ process. On the other hand, $w_{\rm down}$ results from all four processes in which the electron gains the energy ω_0. However, at zero temperature and when $eV \geq \omega_0$ the $R \to L$ process *ceases* to contribute. It follows from Eq. (3) that the stationary vibration population,

$$N_{\rm ho} = \frac{w_{\rm up}}{w_{\rm down} - w_{\rm up}} \ , \tag{4}$$

is independent of the electron-phonon coupling,[29] and vanishes at zero temperature as long as $eV \leq \omega_0$.

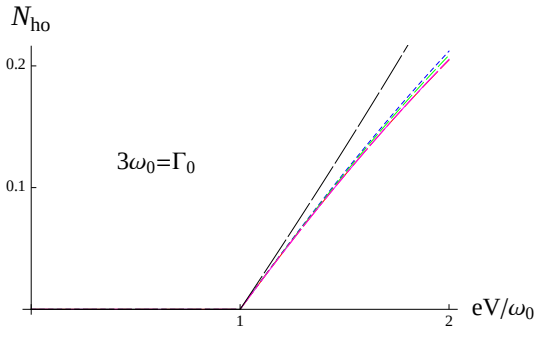

FIG. 1: The population of the oscillator modes, $N_{\rm ho}$, at zero temperature, as a function of eV/ω_0, for various values of the bare transmission: $\mathcal{T}$=0.2 (smallest dash size), 4/17, 0.3, 4/9, and 0.9 (largest dash size). Here $\omega_0/\Gamma_0 = 1/3$.

Figures 1, 2, and 3 depict the nonequilibrium phonon population at zero temperature (see also Ref. 17). The curves are for various values of the bare transmission, $\mathcal{T} = \Gamma_0^2/(\mu^2 + \Gamma_0^2)$, of the junction, The population usually increases with $\mathcal{T}$ and with V, and its magnitude increases with the ratio ω_0/Γ_0.[30] This can be understood qualitatively: since $eV - \omega_0$ is the driving force pushing the population out of equilibrium, $N_{\rm ho}$ increases with the voltage. The increase with $\mathcal{T}$ is due to the fact that the dwell time on the dot, τ_d, increases with $\mathcal{T}$ from being very short off resonance to becoming $\sim 1/\Gamma_0$ around the resonance. As emphasized in Ref. 28, to effectively excite the phonon, τ_d should be longer than the response time of the oscillator (about ω_0^{-1}), i.e., $\Gamma_0 < \omega_0$. Another interesting issue is that the time interval between successive electrons passing the junction, $\tau_c \sim e/I \sim 1/(eV\mathcal{T})$, decreases as $\mathcal{T}$ or eV are enhanced. This too will cause eV to affect more significantly the population at higher values of the bare transmission. However, when $\tau_c < \tau_d$, Pauli constraints between consecutive electrons on the dot should come into play.

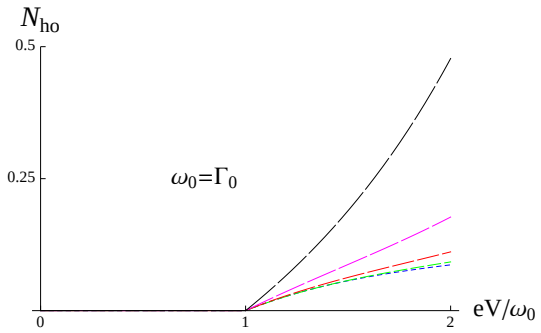

FIG. 2: The same as in Fig. 1, for $\omega_0 = \Gamma_0$.

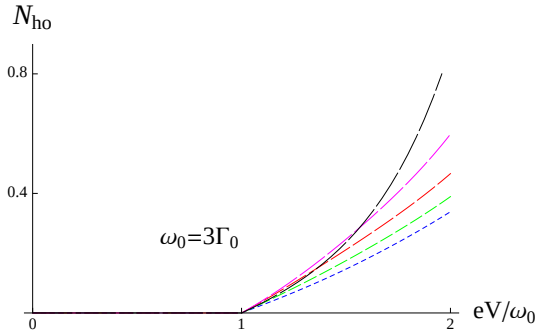

FIG. 3: The same as in Fig. 1, for $\omega_0/\Gamma_0 = 3$.

When $\Gamma_0 \gg \omega_0$, one may estimate the vibration population at finite temperatures by assuming that the bare density of states, [see Eq. (2)], is a constant. Then the stationary population becomes

$$1 + 2N_{\rm ho} = \frac{1}{2}\coth\frac{\beta\omega_0}{2} + \frac{1}{4}\Big(1 + \frac{eV}{\omega_0}\Big)\coth\frac{\beta(\omega_0 + eV)}{2} + \frac{1}{4}\Big(1 - \frac{eV}{\omega_0}\Big)\coth\frac{\beta(\omega_0 - eV)}{2} \ , \tag{5}$$

independent of the bare resonance width Γ_0 and of the band width of the leads. This resembles the magnetization of a Kondo ion out of equilibrium,[29] with the oscillator frequency ω_0 playing the role of the applied magnetic field. (That magnetization is the inverse of $1 + 2N_{\rm ho}$.)

The current flowing through the junction can be presented in the form [see, e.g., Ref. 28]

$$I = e\Gamma_0 \int \frac{d\omega}{2\pi} \mathrm{Im} G^a_{00}(\omega) \Big(f_L(\omega) - f_R(\omega) \Big) \ , \qquad (6)$$

where $\mathrm{Im}G^a_{00}/\pi$ is the density of states on the dot, fully dressed by the interaction with the vibrations. The (advanced) Green function on the junction is

$$G^a_{00}(\omega) = \frac{1}{\omega - i\Gamma_0 - \Delta\epsilon_0 - \Sigma^a_{\rm ho}(\omega)} \ , \qquad (7)$$

where $\Delta\epsilon_0$ is the polaron shift,

$$\Delta\epsilon_0 = -\frac{\gamma^2}{\omega_0} \int d\omega \mathcal{N}(\omega) \Big(f_L(\omega) + f_R(\omega) \Big) \ , \qquad (8)$$

and $\Sigma_{\rm ho}$ is the self-energy due to the electron-phonon processes. Up to second-order in the electron-phonon coupling it reads[28]

$$\Sigma^a_{\rm ho}(\omega) = \frac{\gamma^2}{2} \int d\omega' \mathcal{N}(\omega') \Bigg(\frac{2N_{\rm ho} + \sum_{\alpha=L,R}(1 - f_\alpha(\omega'))}{\omega - \omega_0 - \omega' - i0^+} + \frac{2N_{\rm ho} + \sum_{\alpha=L,R} f_\alpha(\omega')}{\omega + \omega_0 - \omega' - i0^+} \Bigg) \ . \qquad (9)$$

Employing Eqs. (8) and (9) in Eq. (6), we have derived the differential conductance of the bridge, G, at zero temperature, and to second order in the coupling with the phonons.

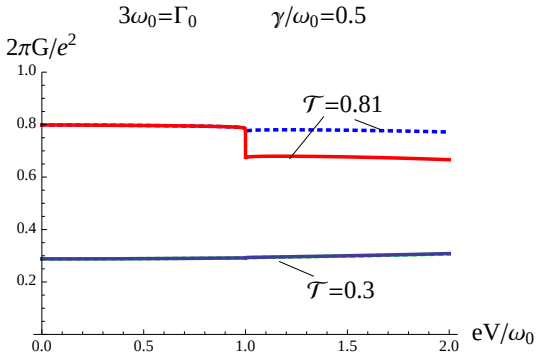

FIG. 4: The zero-temperature differential conductance, as a function of eV/ω_0, for two values of the bare transmission, marked on the figure. The full lines show the conductance with the nonequilibrium phonon population, the dashed curves are with the equilibrium one. Here $\omega_0/\Gamma_0 = 1/3$.

Figures 4, 5, and 6 show several examples of the dependence of the differential conductance on the bias voltage and on the other parameters of the junction. The first figure corresponds to the case where the junction is tightly bound to the leads, and hence the dwell time of the electrons is rather short. Then, at relatively low values of the bare transmission ($\mathcal{T} = 0.3$ in our example) there is no discernible modification in the conductance which is about the same either for nonequilibrium phonon population or for the equilibrium one. However, for higher values of the bare transmission ($\mathcal{T} = 0.81$) the step-down feature of the conductance at threshold for inelastic tunneling is enhanced for nonequilibrium phonons as compared to the equilibrated ones.

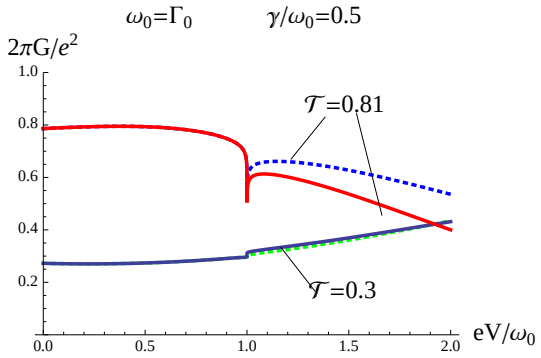

FIG. 5: The same as in Fig. 4, for $\omega_0 = \Gamma_0$.

From the few examples portrayed in Figs. 4-6 we see that when the bare transmission of the junction is high, then the conductance in the presence of nonequilibrium phonons is lower than the one pertaining to the case of equilibrated vibrations. For low bare transmissions the difference is rather small. One notes that the logarithmic singularity associated with the *real* part of the self energy at the channel opening, which has been previously discussed[14,25,28] for an equilibrium population of the phonons, is still manifested also when these excitations are out of equilibrium, for high enough values of the bare transmission of the junction.

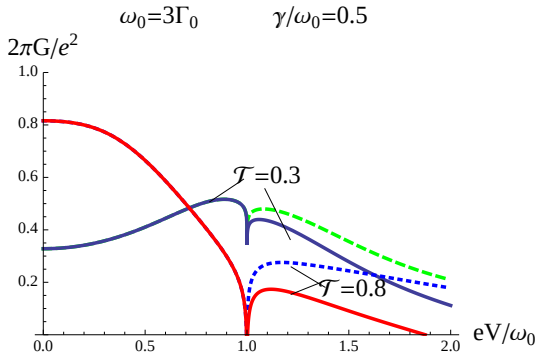

FIG. 6: The same as in Fig. 4, for $\omega_0 = 3\Gamma_0$.

The fact that the changes in the differential conductance which are associated with the type of the vibration population, $N_{\rm ho}$, are more pronounced for the larger ω_0/Γ_0 ratio is connected with the actual value of $N_{\rm ho}$, see Figs. 1-3. The electrons pump more and more excitations into the higher vibrational states as the bias voltage increases and this pumping is more effective as the dwell time exceeds considerably the response time of the oscillator.

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[30] In some cases, $N_{\rm ho}$ does not increase monotonically with V or with $\mathcal{T}$. However, this is a small effect, occuring mainly at relatively small V.